

A solid oxide fuel cell and a carbon direct-oxidizing-type electrode for the fuel cell

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Abstract of GB2278010

There is disclosed a solid oxide fuel cell and a carbon direct-oxidizing-type electrode for the cell. The fuel cell comprises vanadium carbide being used as the fuel electrode, and the vanadium carbide and a carbon-series fuel serve both as an electrode and as a fuel.

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A solid oxide fuel cell and a carbon direct-oxidizing-type electrode for the fuel cell

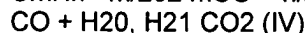
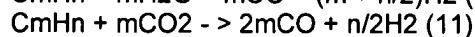
Description of GB2278010

A SOLID OXIDE FUEL CELL AND A CARBON DIRECT-OXIDIZING-TYPE ELECTRODE FOR THE FUEL CELL FIELD OF THE INVENTION

The present invention relates to a solid oxide fuel cell (solid electrolyte-type fuel cell) wherein a carbon-series fuel, such as coal and charcoal, is partially oxidized without requiring any gasifying step or a fuel-reforming step, and the partial oxidation reaction is used as a fuel cell reaction, that produces free energy that can be converted to electrical energy. The present invention further relates to a fuel electrode that has a catalytic action for directly oxidizing carbon-series fuels in solid oxide fuel cells.

BACKGROUND OF THE INVENTION

In a fuel cell, for example, of a phosphoric acid electrolyte-type, an alkali electrolyte-type, or a solid polymer electrolyte-type, natural gas, petroleum, or coal, which serves as a raw fuel, is used in a gasifying-and-reforming reaction step provided by combining reforming reactions (I) and (II), which are endothermic reactions, with an exothermic reaction (III), and by then converting all of the mixed gases of carbon monoxide and hydrogen that have been converted into hydrogen by the shift reaction (IV).



In molten carbonate cells and oxide fuel cells, which are high-temperature fuel cells, the shift reaction (IV) can be omitted, but in these cells a raw fuel is introduced after it is first converted to a mixed gas of hydrogen and carbon monoxide, by the reactions (I) to (III). Since in these conventional fuel cells, the step of gasifying and reforming the raw fuel and the fuel cell step are separate steps, the whole system is complicated, and therefore it has been pointed out that there is a defect in that the efficiency, for example, of heat recovery is low.

In order to obviate this defect, recently, a direct internal reforming method has been studied, wherein the partial oxidation reaction (III) is not required by incorporating the fuel-reforming step, which is an endothermic reaction, in the fuel cell stack in which an exothermic reaction takes place. This enables recovery of at least the fuel loss that occurs with the reaction (III). In this direct internal reforming method, the activity of the electrode, made up mainly of nickel, that is conventionally used decreases conspicuously, and in order to restrict this decreasing of activity, it is necessary to add a large amount of water. However, because heat flows in and out with the evaporation and condensation of this added water, the efficiency of the whole system, including the efficiency of heat exchange, is considerably reduced.

Although natural gas has been studied with respect to the direct internal reforming method, hydrocarbon fuel, naphtha, and coal, which have higher molecular weights, have not yet been studied. This is because with use of long-chain hydrocarbons, such as naphtha, in the direct internal reforming method, deposition of carbon is remarkable and the nickel fuel electrode cannot be prevented from being poisoned and deactivated even if a large amount of steam is introduced.

Therefore, since coal's carbon ratio is higher than that of naphtha, the direct internal reforming method using coal as a raw fuel has been considered as a matter of course impossible.

Further, when coal is used as fuel, the conditions of operation of the conventional coal gasifying method require a pressure and a temperature far higher than those of solid oxide fuel cells that are operating at a highest temperature, and therefore it is also required that the coal gasifying step and the fuel cell step be separated into separate plants in making up a powergeneration system. As a result, for example, it was not possible for the heat generated by solid oxide fuel cells to be fed back for effective utilization in the process of coal gasification, and therefore, when coal was used as fuel, only a lower generation efficiency was obtained in comparison with the use of natural gas or the like.

As one solution to the above problems, a coal gasifying apparatus and a fuel cell are made into a complex plant. To do so requires a fuel cell into which coal can be introduced directly or a fuel cell that can be installed in a coal gasifying apparatus. Further, as a fuel electrode for such a fuel cell, a fuel electrode made of a new material is required which material is not poisoned and deactivated, unlike the above-mentioned nickel electrode is, even when it comes in direct contact with coal. However there are no conventional fuel electrodes that satisfy this requirement.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a material for an electrode that will not be poisoned with carbon and an electrode comprising that material.

Further, another object of the present is to provide a solid oxide fuel cell high in efficiency, wherein even a carbon-series fuel, such as coal, from which it is conventionally difficult to attain high efficiency of generation of electric power can be subjected to a direct oxidation combustion reaction without carrying out a gasifying step separately and electric power can be generated from the gasifying step itself.

Another object of the present invention is to provide a direct internal-reforming-type fuel cell wherein a small amount of steam needs to be introduced, or on the other hand introduction of steam may not be required.

Other and further objects, features, and advantages of the invention will appear more evident from the following description, taken in connection with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a cross section showing an embodiment of the solid oxide fuel cell of the present invention.

Fig. 2 is the electric current-voltage characteristic curves obtained when the solid oxide fuel cell which used different carbides as a carbon directoxidation electrode, was anodically polarized (to the direction of oxidation).

Fig. 3 is the phase equilibrium chart of the V-C-O type at 1273 K, wherein the logarithm of the oxygen partial pressure is plotted along the abscissa axis and the logarithm of the carbon monoxide partial pressure is plotted along the ordinate axis.

Fig. 4 is a conceptional diagram of the oxidation reaction at the interface between a vanadium carbide electrode and an yttria-stabilized zirconia electrolyte.

Fig. 5 is the electric current-voltage characteristic curves obtained when the solid oxide fuel cell which used a combination of vanadium and graphite, only graphite, and only Taiheiyo coal (name of Japanese domestic coal), as a carbon direct oxidation electrode was polarized anodically.

Fig. 6 is a graph showing the relationship between the concentration of the discharged carbon monoxide and the generated electric current in a solid oxide fuel cell that used a vanadium carbide electrode.

DETAILED DESCRIPTION OF THE INVENTION

The inventors have keenly studied in various ways to attain the above objects and have found that as a material for a fuel electrode of solid oxide fuel cells that use a carbonaceous fuel, such as coal, vanadium carbide can be used without it being poisoned and deactivated. Further, it has been found that when the solid oxide fuel cell is made into the shape of a cylinder, fuel in a solid form, such as coal powder, can be directly introduced, and a fuel gasification-fuel cell complex reaction system can be completed wherein the partial oxidation reaction of the gasifying step itself of the fuel in the form of solid is made serve as a fuel cell power generation reaction. The present invention has been made based on these findings.

That is, the present invention provides:

- (1) A solid oxide fuel cell, which comprises using vanadium carbide in the fuel electrode;
- (2) The fuel cell as stated in above (1), wherein the vanadium carbide and a carbon-series fuel are used as the fuel electrode and a fuel;
- (3) The fuel cell as stated in above (2), wherein natural gas or naphtha is reformed;
- (4) The fuel cell as stated in above (2), wherein the carbon-series fuel is coal and the partial oxidation reaction and gasification reaction of the coal serve as a power-generation reaction of the fuel cell; and

(5) A fuel electrode for a solid oxide fuel cell, which comprises vanadium carbide.

Now the present invention will be described in detail.

In the present invention, the term "carbonseries fuel" refers to a carbon fuel, such as graphite, as well as to a usual hydrocarbon fuel, such as coal, natural gas, and naphtha. Further, the term "reforming" refers to a catalytic action that converts high molecular weight hydrocarbons to useful low molecular weight hydrocarbons, using the fuel cell of the present invention.

Specifically, for example, naphtha, which is a mixture of low-boiling hydrocarbons obtained by distilling petroleum, coal tar, or the like, is intended to convert to methane, ethylene, ethane or the like, and further to convert to CO and H₂.

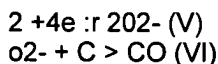
In the present invention, as the solid electrolyte of the solid oxide fuel cell, zirconia is preferable and yttria-stabilized zirconia is more preferable.

The embodiments of the present invention are described with reference to the drawings:

Fig. 1 is a cross section of a carbon directoxidation solid oxide fuel cell according to the present invention; and Fig. 2 shows the results of measurement of activity of various electrodes in the fuel cell of Fig. 1.

In Fig. 1, reference numeral 1 indicates a tube of yttria-stabilized zirconia, 2 indicates a fuel electrode made of a mixture of a graphite powder and compound to be measured, 3 indicates a graphite pellet for pressing the mixture 2, 4 indicates an electrode coated with platinum (counter electrode) for air, 5 indicates a reference electrode, 6 indicates a rod made of graphite, 7 indicates an alumina tube, and 8 and 9 are an inlet and outlet of a carrier gas, respectively.

As shown in Fig. 1, the measurement was carried out in the fuel cell wherein the powder mixture 2 was placed in the tube 1 and electric current was collected with the rod 6. According to this fuel cell, oxygen is converted into oxide ions on the air side; these ions diffuse into the zirconia; and react on the graphite side, to oxidize the graphite. That is, the following reactions (V) and (VI) proceed respectively on the air side and the fuel side, and a part of free energy is generated as electricity. The generation of the carbon monoxide (CO) was measured by gas chromatography.



In the measurement, wolfram carbide (WC), zirconium carbide (ZrC), or vanadium carbide (VC) was used in the mixture with graphite.

In Fig. 2, the abscissa axis represents electric potential using air as reference and the ordinate axis represents the electric current obtained from the cell, showing that the larger the obtained electric current is the higher the generation efficiency is. From Fig. 2, it can be understood that electric current itself can be obtained from almost all compounds used in the mixture.

However, when vanadium carbide is used in the mixture as an electrode, electric current remarkably larger than that in the case of other compounds is obtained, indicating that a higher generating efficiency can be obtained by using vanadium carbide in the electrode.

In the present invention, the description "vanadium carbide is used as a fuel electrode" means that vanadium carbide is contained together with a carbonseries fuel, and although there are no particular restrictions on the mixing ratio of vanadium carbide and a carbon-series fuel, preferably the larger the amount of vanadium carbide, the more favorable it is. The amount of vanadium carbide is generally 40 wt% or more, preferably 50 wt% or more, and particularly preferably 80 wt% or more, based on the total amount of the vanadium carbide and the carbon-series fuel.

In another embodiment of the present invention, the fuel electrode and the air electrode shown in Fig. 1 are placed outside and inside, reversing the structure of

Fig. 1. For example, an yttria-stabilized zirconia tube serves as a solid electrolyte, and on its inside inner wall is provided an electrode of platinum, silver, perovskite, or the like as an air electrode. Air or concentrated oxygen is fed to the air electrode side, and a fuel-electrode mixed powder made up of vanadium carbide powder dispersed in coal powder, which mixed powder is held in a prescribed container, is provided outside the zirconia tube, thereby constituting a carbon directoxidation fuel single cell. In this

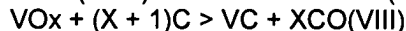
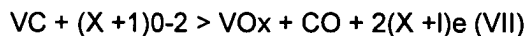
case, the oxygen fed inside the tube is changed into oxide ions; these ions pass through the zirconia tube, to oxidize the coal powder positioned outside, and the free energy of that oxidation reaction is taken out as electric power.

Further, such single cells may be connected in series or in parallel through an electrical connecting material or interconnection, to form a bundle of cells.

The bundle may be placed in a container, and if air is supplied to the inside of the tube and powder coal is supplied to the outside, a coal gasifying apparatus-fuel cell can be made.

To elucidate the action of a vanadium carbide, thermodynamic analysis was carried out. That is, on the fuel cell fuel electrode side, where the above-described zirconia was used, the existent form of the vanadium carbide was estimated from the thermodynamic equilibrium calculation. Fig. 3 shows the phase equilibrium chart of the V-C-O system at 1,000°C, wherein the abscissa axis represents the logarithm of the oxygen partial pressure and the ordinate axis represents the logarithm of the carbon monoxide. According to this phase equilibrium chart, oxide phases, such as V₂O₃, V₃O₅, V₄O₇, V₅O₉, V₁₀O₁₉, and V₂O₄, appear successively from around an oxygen partial pressure of 10⁻¹⁰ atm toward the higher oxygen partial pressure side. Therefore, based on the equilibrium calculation, it is strongly surmised that the oxide ions that pass through the zirconia probably oxidize not carbon but vanadium carbide.

The oxidized vanadium carbide is converted to the above vanadium oxide (VO_x), and at that time instead of the reaction (IV), the reaction (VII) proceeds. It can be surmised that the produced vanadium oxide is reduced with the coexistent carbon by the reaction (VIII), to return to vanadium carbide, to recycle, so that thereby the fuel cell reaction may take place.



Such a conceptual diagram is shown in Fig. 4.

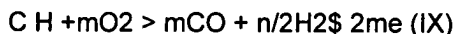
The vanadium carbide electrode reacts with the oxide ions that pass through the zirconia solid electrolyte, to become vanadium oxide, and this oxide supplies oxygen to the carbon of the fuel, to promote the oxidation reaction.

After it supplies oxygen, the vanadium oxide becomes the carbide again.

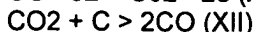
The conventional electrode, such as nickel, for fuel promotes oxidation of the fuel without being changed itself by oxidation and reduction and acts to allow electrical charges to move, thereby collecting electricity. However, in the vanadium carbide electrode of the present invention, the oxidation of fuel seems to be carried out through the oxidation and reduction of the vanadium carbide. In other words, it can be said that the zirconia surface and the graphite rod used for collecting electricity are electrodes and vanadium carbide serves rather as the fuel.

Thus, since the vanadium carbide itself reacts with carbon and oxygen, unlike the nickel electrode, the vanadium carbide is not denatured or is not changed in its form to be poisoned and deactivated when it comes in contact with carbon.

Now, the action of the case in which a carbon system fuel, coal in this instance, is applied to the solid oxide fuel cell having the above vanadium carbide electrode, is described. By supplying a composite system of an electrode and a fuel formed by mixing vanadium carbide and coal powder to the fuel electrode side of the cylindrical solid oxide fuel cell, and supplying air to the counter electrode, a fuel cell can be made up that involves reactions (IX) and (X) through the reactions (VII) and (VIII).



The reason the reaction (XI) does not follow the reaction (X) is considered to be because, even if carbon monoxide is oxidized to carbon dioxide (XI), the reaction (XII) occurs due to the excess presence of carbon, and the carbon dioxide is reduced again to carbon monoxide.



Accordingly, in the fuel cell of the present invention, it can be said that the partial oxidation reaction (III) in

the coal gasifying reaction is utilized as a fuel cell reaction. That is, the products of this fuel cell are electric power and coal gas. In other words, the fuel cell is a coal gasifying apparatus that functions as a fuel cell, and, in that fuel cell, electric power is also generated from the coal gasifying step, so the results increase efficiency of the coal gasification fuel cell system.

Further, if, instead of the coal powder-vanadium carbide powder, only vanadium carbide is loaded into the above apparatus and a gaseous fuel, such as natural gas, is directly introduced into the apparatus, it is apparent that a fuel cell that includes the reactions (V) and (VI), based on the above-described action, can be made up. In this fuel cell, even if a large amount of steam is not supplied, the performance of the vanadium carbide electrode is not lost, and therefore direct reforming is made possible without the introduction of steam.

According to the solid oxide fuel cell of the present invention, electric power can be generated even from the gasifying step itself of a carbon- system fuel and therefore the efficiency of power generation can be elevated considerably over the conventional fuel cells.

Further, a carbon-series fuel, such as coal, charcoal, and natural gas, can be directly oxidized and reformed without gasifying it.

The electrode containing vanadium carbide of the present invention exhibits satisfactory active catalytic behavior in a solid oxide fuel cell, wherein carbon can directly be oxidized and combusted, and the electrode can remarkably increase generation power of the cell.

Further, the electrode can not only increase the current intensity, it can also be used in a fuel cell in which a carbon-series fuel can be directly oxidized without a reforming step, to thereby to remarkably increase the power-generation characteristics.

The present invention will now be described in detail with reference to the following examples, but the invention is not limited to them.

Example 1

A fuel cell was made up in accordance with Fig.

1. In this cell, for the solid electrolyte, zirconia stabilized with 8 mol% of Y2O3 (yttria) was used. A mixed powder (2) made up of about 3 g of vanadium carbide and about 3 g of graphite was placed in the zirconia tube 1 (length: about 300 mm, diameter: 21 mm, thickness: about 2 mm), one end of which was closed, and the powder 2 was pressed by a graphite pellet 3. The lower outer surface of the closed end of the zirconia tube 1 was coated with a platinum paste, to prepare a counter electrode (cathode) 4. The reference electrode 5 was a platinum wire wound around the side wall surface of the zirconia tube, and air was used as standard. The working electrode (anode) was the vanadium carbide-graphite mixture 2 placed in the zirconia tube, and the electrode area was about 3 cm².

Since the platinum wire is not resistant to carbon, a graphite rod 6 was used to collect electricity from the working electrode. During the elevation of the temperature of the fuel cell and during the electrochemical measurement, Ar (argon) was flowed at a rate of about 60 ml/min, as a carrier gas to evaluate the gas in the fuel cell. Reference numeral 7 indicates an alumina tube for protecting the graphite rod.

Further, for comparison, a fuel cell was formed in which the composition of the fuel electrode was changed.

The current-voltage characteristics of the above fuel cells measured under the above conditions are shown in Figs. 2 and 5. Fig. 2 shows the results of measurement of the cases of cells in which the vanadium carbide in the mixed powder 2 was changed to other carbides, or only graphite, together with the results of measurement of the case of the present invention. Fig. 5 shows the results of tests of cells in which, instead of the above mixed powder 2 of vanadium carbide and graphite, only graphite powder or only Taiheiyō coal (Japanese domestic coal) was used. In the measurement, a potentiostat (a constant potential-controlling apparatus) was used to keep the electric potential constant for a certain period of time (30 sec), and at that electric potential the electric current intensities were plotted.

As is apparent from Fig. 2, generally when a carbide powder was mixed with graphite in an electrode, higher electric current intensities were shown in comparison with when only graphite was used. Among the

carbide electrodes, in particular vanadium carbide showed a higher electric current intensity, and a sharp increase in electric current intensity was observed from the anodically polarized point of about 500 mV (in the direction of oxidation). The maximum electric current intensity was about 1000 mA. From this it can be understood that, when vanadium carbide was used, a remarkable increase in electric current intensity occurred and the efficiency of the power generation was high. From Fig. 5 it can be understood that a high electric current intensity only be attained when vanadium carbide was used in combination with graphite.

Example 2

With respect to the fuel cell prepared in

Example 1, which had a mixture of vanadium carbide powder and graphite powder, the gas discharged from the cell was analyzed by gas chromatography and was compared with the electric current-voltage curve. The relationship between the volume fraction of CO (carbon monoxide) contained in the discharged gas and the output electric current is shown in Fig. 6. Due to the structure of the cell, when CO₂ was produced at the electrode/electrolyte interface, the above reaction (XII) took place during the passage of the CO₂ through the carbon fuel, and only CO was detected.

However, the total amount (coulomb amount) of electrical energy produced by the oxidation combustion of the carbon did not change even if the reaction according to the formula (XII) took place. Therefore, the coulomb electric amount to be obtained from the produced amount of CO was calculated and was plotted in Fig. 6. From this, it can be understood that there is a rough mutual relationship between the measured values and the calculated values. Therefore, it can be understood that the output electric current of the fuel cell of the present invention is due to the oxidation combustion of carbon.

Example 3

A cell was prepared in the same manner as

Example 1, except that, as the fuel electrode, a mixed powder of about 3 g of vanadium carbide and about 3 g of

Taiheiyo coal (Japanese domestic coal) was used. As a carrier gas, Ar (argon) was flowed through the cell at a rate of about 60 ml/min; the electrical potential was kept constant by a potentiostat at 1273 K for a certain period of time (30 sec); and when the electric current intensity was measured at that electric potential, a maximum electric current intensity of 900 mA was obtained. At an electric potential of about -100 mV (an anodically polarized electric potential of about 900 mV) for air, an electric current intensity of about 800 mA was obtained.

The electric current-voltage curve was approximated a straight line.

Having described our invention as related to the present embodiments, it is our intention that the invention not be limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

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A solid oxide fuel cell and a carbon direct-oxidizing-type electrode for the fuel cell

Claims of **GB2278010**

WHAT WE CLAIM IS:

1. A solid oxide fuel cell, which comprises using vanadium carbide in the fuel electrode.
2. The fuel cell as claimed in claim 1, wherein the vanadium carbide and a carbon-series fuel, used as the fuel electrode, serve both as an electrode and a fuel.
3. The fuel cell as claimed in claim 2, wherein natural gas or naphtha is reformed.
4. The fuel cell as claimed in claim 2, wherein the carbon-series fuel is coal and the partial oxidation reaction and gasification reaction of the coal serve as a power-generation reaction of the fuel cell.
5. A fuel electrode for a solid oxide fuel cell, which comprises vanadium carbide.
6. The fuel cell as claimed in claim 1, wherein a yttria stabilized zirconia compound is used as a solid electrolyte of the fuel cell.

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